Isotopic Techniques for Assessment of Groundwater Discharge to the Coastal Ocean

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LONG-TERM GOALS

One of the persistent uncertainties in establishing marine geochemical mass balances is evaluating the influence of submarine groundwater discharge (SGD) into the ocean. Our long-term goal is to develop geochemical tools (e.g., radon and radium isotopes) to quantify the magnitude of SGD on a local to regional scale. Improvements in field-based analytical devices is sought in order to allow evaluations on more time efficient basis. Since there is no standard methodology for measurement of groundwater flow into the ocean, we are actively involved in coordinating and participating in assessment intercomparisons.

OBJECTIVES

We are setting out to test the following hypotheses: (i) the apparent discrepancy between groundwater flux results based on geochemical tracing and hydrological modeling (Burnett et al., 2002) arises because the tracers are measuring <u>total flow</u> while the models are only accounting for the <u>fresh water</u> component of that flow; (ii) the radon tracing model can be much better constrained by the combining use of radon and short-lived Ra-isotopes (^{223}Ra and ^{224}Ra) to independently derive a near-shore mixing rate; and (iii) the most efficient manner to evaluate the quality of SGD assessment methodologies is by direct intercomparisons of independent approaches.

APPROACH

Radon is a good natural tracer of SGD because its concentration is very high in groundwater but low in seawater, it behaves conservatively, and it is relatively easy to measure. Assessment of possible temporal trends of radon is important because groundwater flow is known to be extremely variable — in some cases even reversing direction in response to external forcing (tides, change in water table height, etc.). Radium isotopes are also very useful as natural tracers and can complement the radon investigations. Our approach during this project is: (1) to develop further our continuous Rn monitor and implement the use of Ra isotopes; and (2) to test these systems in the field in different environments and over different time scales to evaluate short (tidal) to long-term (seasonal) patterns.

The main principle of using continuous radon measurements to decipher rates of SGD is to convert changes observed in Rn inventories over time to fluxes by monitoring the inventory of ^{222}Rn over time, making allowances for losses due to atmospheric evasion and mixing with low concentration waters offshore (**Fig. 1**). Although changing radon concentrations in coastal waters could be in response to a number of processes (sediment resuspension, long-shore currents, etc.), we feel that advective transport of Rn-rich groundwater (pore water) through sediment is typically the dominate process. Thus, if one can measure or estimate the radon concentration in the advecting fluids, we can easily convert ^{222}Rn fluxes to water fluxes.

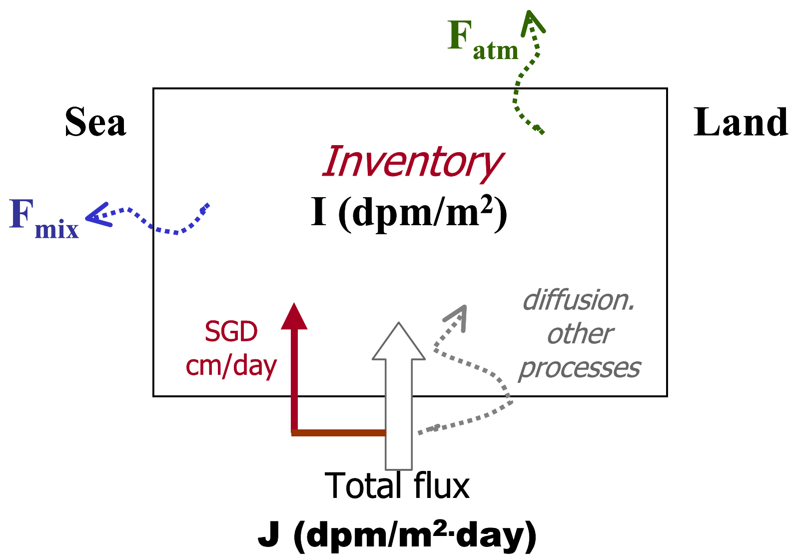

Figure 1. Conceptual model of use of continuous Rn measurements for estimating SGD. [The inventory refers to the total amount of ^{222}Rn per unit area. Decay is not considered because fluxes are evaluated on a very short time scale relative to the half-life of ^{222}Rn.]

WORK COMPLETED

During the last year we have added the capability of analyzing all four naturally occurring radium isotopes and we have continued to make improvements on our continuous radon monitor. The exchanger part of the system has been improved by testing several types of spray nozzles to optimize the flow rates and emanation of radon. Testing and evaluation of the isotopic approach (radon and radium isotopes) over the past year has been done at the Florida State University Marine Laboratory (FSUML; karst, coastal plain geology), Apalachicola Bay (estuary), Florida Bay (karst), Sao Paulo coast of Brazil (fractured crystalline rocks), southeast coast of Sicily (limestone, volcanic), and Shelter Island, New York (glacial till). Many of these experiments were done in collaboration with a large team of investigators employing many different techniques to evaluate groundwater discharge.

RESULTS

We review here some of the highlights from the experiments at FSUML and Shelter Island. We performed our first seasonal experiment at FSUML (Gulf of Mexico) from Sept. 28 to Oct. 3, 2001. After normalizing to a mean tidal height and correcting for supported radon and estimated atmospheric losses, we calculated the net ^{222}Rn fluxes over this interval (**Fig. 2**). These fluxes are clearly not in steady state but fluctuate with an apparent period of approximately 12 hours, reflecting some dependence on the mixed, semi-diurnal tides in this region. Apparent negative fluxes also occur which we assume is due to mixing. The dashed line shown in the figure is our estimate (thought to be conservative) of the loss caused by mixing of nearshore (high radon) waters with offshore (low radon) seawater.

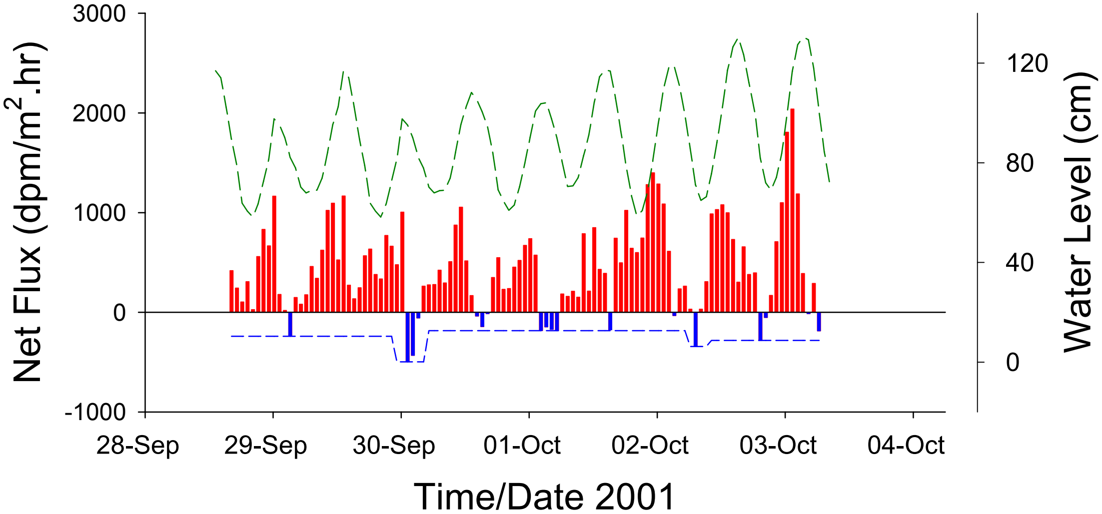

Figure 2. Net radon flux (bars: left scale;dpm/m^2.hr) and water level (dashed line: right scale) vs. time based on continuous Rn measurements at FSUML from Sept. 28 to Oct. 3, 2001.

We also collected a transect of samples at 9 stations (3 duplicate samples, so n=12) extending from nearshore out to approximately 5 km offshore and then measured the activities of both the short-lived (^{223}Ra and ^{224}Ra) and long-lived (^{226}Ra and ^{228}Ra) isotopes of radium. The distribution of the short-lived radium species will depend on two processes, decay and mixing. Since the decay rates are known precisely (^{223}Ra and ^{224}Ra have half-lives of 11 and 3.5 days, respectively), the mixing rates can be estimated based on the slope of the activity versus distance plot (**Fig. 3a**). Using the methodology of Moore (2000) a regression of all data points from the maximum in ^{223}Ra (located near a submarine spring) seaward provides an estimated mixing coefficient of 18±6 m^2/sec. Multiplying the gradient in the measured ^{226}Ra concentration over the same distance (-180 dpm/m^3.km; **Fig. 3b**) by this mixing term provides the offshore flux of the groundwater tracer. This may then be divided by the estimated groundwater Ra concentration to derive a water flux.

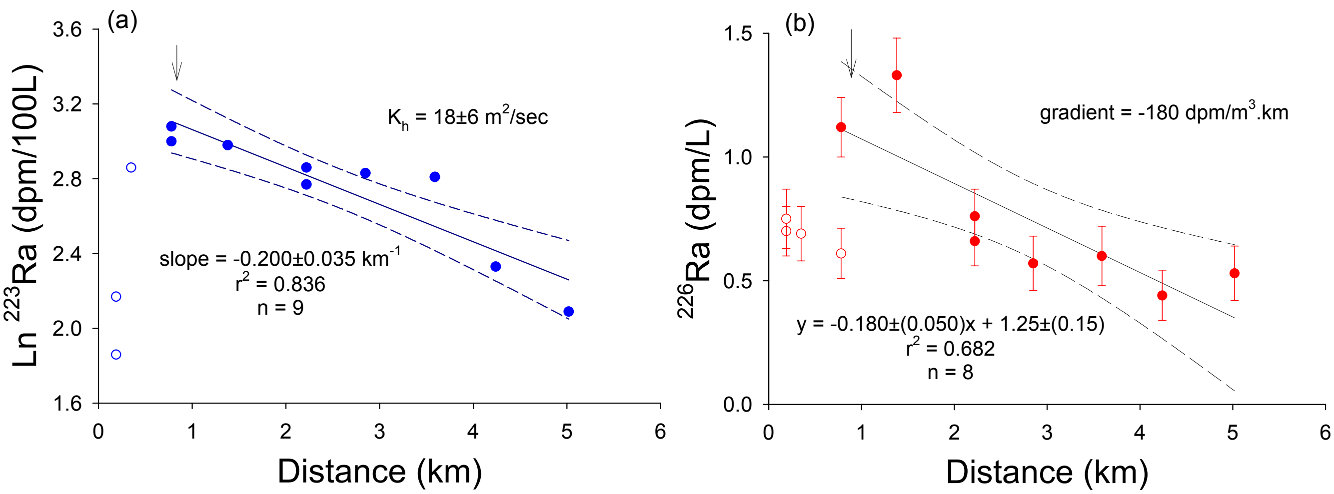

Figure 3. (a) Variation of Ln ^{223}Ra versus distance offshore from the FSU Marine Laboratory, October 2, 2001; (b) ^{226}Ra vs. distance along the same transect as "A". [Most Ra enters from a submarine spring (approximate location shown by arrow)]

One of the benefits in applying both the continuous radon and radium isotope approaches to the same system is that we can use the mixing coefficient derived from the short-lived radium to make an independent estimate of the radon loss due to mixing. We estimated the total radon flux (390 dpm/m^2.hr) by multiplying the gradient in the ^{222}Rn concentration along the inshore-to-offshore transect by the mixing coefficient derived from the ^{223}Ra gradient and the average depth and normalizing to the width of the assumed seepage face. This compares very favorably to our variable mixing fluxes, assigned by inspection of the "net" benthic ^{222}Rn fluxes (Fig. 2) that ranged from 180-500 dpm/m^2.hr with an average of 240 dpm/m^2.hr. The overall estimates of SGD by both the Rn and Ra models were similar at 20-29 and 43 m^3 per meter width of shoreline per day, respectively.

We participated in a SCOR/LOICZ/IOC sponsored SGD intercomparison exercise on Shelter Island, New York (May 17-24, 2002). Shelter Island (~28 km^2) is located in the Peconic Bay between the north and south forks of Long Island (**Fig. 4**). The island is sparsely populated and only a small section in the northwestern area of the island has a storm drainage system. Therefore, precipitation evaporates, transpires, or recharges the freshwater aquifer. There are no major streams or creeks on the island and therefore, groundwater that enters the aquifer primarily discharges through the coastline into the surrounding waters. The island is composed of upper Pleistocene glaciofluvial deposits (Soren, 1978), consisting of outwash sands and drift that form high hills. Numerical modeling of groundwater flow based on a series of monitoring wells indicates that groundwater flow discharges at high velocities ranging from 60 to 240 cm/day in the West Neck Bay area.

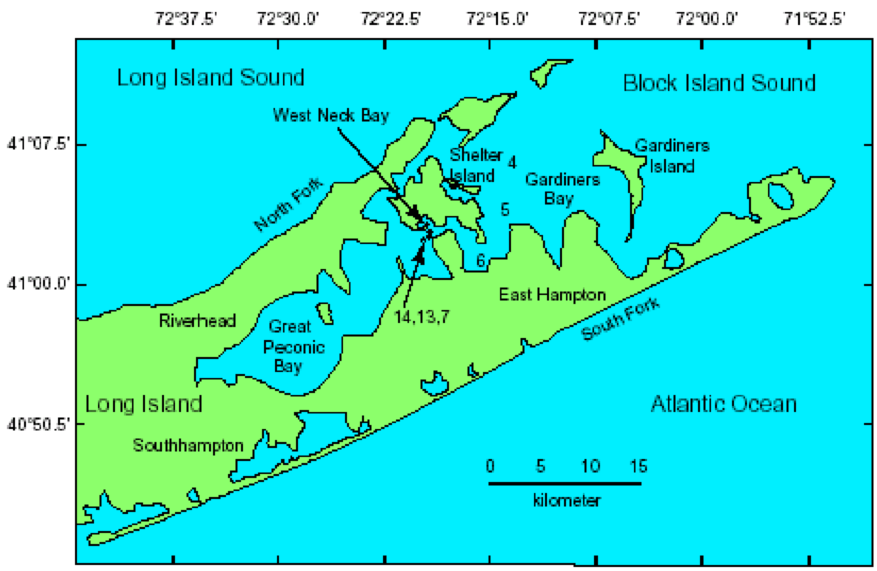

Figure 4 Location map of West Neck Bay, the study site located on Shelter Island, New York. [The numbers refer to station locations for collection of water samples for geochemical tracers.]

In addition to use of our continuous radon monitor, we collected several samples in a line from West Neck Bay and into Gardiner's Bay for analysis of radium isotopes to evaluate mixing and estimate SGD by calculating the flux of long-lived radium (which must be balanced by input from groundwater as there are no significant surface water sources in the area). We used an approach proposed by Moore (2000) and recently used by Kelly and Moran (2002) to estimate the residence times of coastal waters. If one assumes that the source of short-lived radium isotopes is groundwater with a constant isotopic composition, then:

$$^{224}Ra_{obs} = {}^{223}Ra_{obs}\left(\frac{^{224}Ra}{^{223}Ra}\right)_i \bullet \frac{e^{-\lambda_{224}T}}{e^{-\lambda_{223}T}}$$

where $(^{224}Ra/^{223}Ra)_i$ represents the initial activity ratio and T is the residence time. Once an initial ratio is established, the residence time may be estimated by plotting the observed isotopic data, ^{224}Ra versus ^{223}Ra, together with isolines for theoretical values of T (**Fig. 5a**). We analyzed water collected from seepage meters (n=9) and pooled these results as an estimate of the initial ratio (13.7). Using this value, the West Neck – Gardiner's Bay system appears to have a residence time of ~5.5 days (**Fig. 5b**).

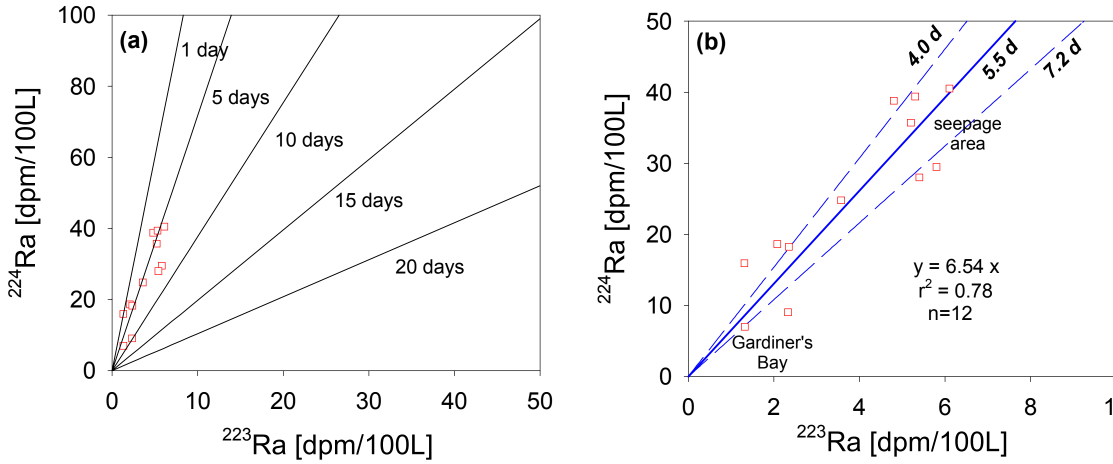

Figure 5 (a) Water mass residence time as a function of ^{224}Ra/^{223}Ra ratios in an embayment assuming input of Ra with a constant initial ratio. (b) Data from Shelter Island, NY (Fig. 4). [These results suggest that the residence time of West Neck Bay is between 4.0 to 7.2 days.]

IMPACT/APPLICATION

The radon monitor has proven to be successful for the continuous measurements of radon in low activity coastal seawater. The addition of radium isotopes has strengthened the overall approach by providing independent SGD estimates and by constraining the mixing loss term in the Rn model. In addition, the radium isotopes may provide a useful method for estimating the flushing time of embayments.

TRANSITIONS

Many of the field experiments we participated in were organized by a SCOR/LOICZ Working Group (http://www.jhu.edu/~scor/wg112.htm) on SGD. That group will now continue through sponsorship from Unesco's IOC (see next section).

RELATED PROJECTS

We are playing a leading role in the IOC program "Assessment and Management Implications of Submarine Groundwater Discharge Into the Coastal Zone" (SGD link on http://ioc.unesco.org/icam/). This 5-year program intends to: (1) develop, test, and standardize methodologies for assessment of SGD into the coastal zone; and (2) evaluate the management implications of SGD and provide appropriate training for coastal zone managers via ICAM (Integrated Coastal Area Management).

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